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NBS/EPA CERTIFIED REFERENCE MATERIAL PERFORMANCE AUDIT PROGRAM: STATUS REPORT 2

by

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16. ABSTRACT

A traceability procedure has been established which allows specialty gas producers to prepare gaseous pollutant Certified Reference Materials (CRM's). The accuracy, stability and homogeneity of the CRM's approach those of NBS Standard Reference Materials (SRM's). Part of this procedure is an independent quality assurance audit of each CRM batch by an EPA-coordinated auditor. As of October 1986, 36 candidate batches had been audited. In general, the agreement between the producer's analytical results and the audit results have been within ± 0.5% relative. Additional data suggest that CRM's are stable during their two-year certification periods.

The purchaser of a CRM is assured that its accuracy is high because of four features of the CRM program:

1. The general technical procedure for producing and analyzing CRM's has been specified by NBS;
2. CRM's are directly traceable to SRM's which are used as reference standards during the analysis of CRM's;
3. The producer's analytical results are verified by measurements which are performed by an independent auditor; and
4. Both the producer's and the auditor's analytical results must be reviewed and approved by NBS before the CRM's may be sold.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has the responsibility for assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the agency, including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Enforcements.

The use of high-accuracy, gaseous calibration standards has been recognized as an integral part of quality assurance programs for air pollution measurement systems. The need for such standards has led to the creation of NBS Standard Reference Materials and NBS/EPA Certified Reference Materials. The Quality Assurance Division of EPA's Environmental Monitoring Systems Laboratory has established a performance audit program for Certified Reference Materials. This program assures the accuracy of these standards. This report describes the current status of the program. It includes a summary of the procedures for producing and auditing the standards as well as a summary of all audits that have been conducted to date.

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ABSTRACT

U.S. Environmental Protection Agency (EPA) regulations for ambient air quality and mobile source emission measurements allow gaseous pollutant calibration standards to be traceable to Certified Reference Materials (CRMs). CRMs are prepared and analyzed by specialty gas producers. The performance audit program for CRMs has been established by EPA and the National Bureau of Standards to help assure the accuracy and stability of CRMs. This report discusses the program and compares producer and auditor results for 36 batches of CRMs. The mean absolute value of the agreement between the two sets of results is 0.18 percent relative, with a maximum of 0.60 percent relative. These data demonstrate that specialty gas producers can prepare and analyze CRMs with a high degree of accuracy. An informal stability study was conducted by RTI which involved the reanalysis of nine previously audited CRMs. The times between the original audits and the reanalysis ranged from 11 to 25 months. The mean absolute value of the concentration change is 0.16 percent relative, with a maximum of 0.29 percent relative. These data suggest that CRMs remain stable throughout their two-year certification period.

This report was submitted in fulfillment of Contract No. 68-02-4125, Work Assignment 98, by the Research Triangle Institute under the sponsorship of EPA. This report covers the period from October 1984 to May 1986.

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SECTION 1

INTRODUCTION

The legal implications of many environmental measurements make it necessary that accurate and stable standards be used to calibrate the monitoring instrumentation. In the past, U.S. Environmental Protection Agency (EPA) regulations have required that gaseous pollutant calibration standards for ambient air quality measurements be traceable to National Bureau of Standards (NBS) Gaseous Standard Reference Materials (SRMs) (1,2). Similarly, calibration standards for mobile source emission measurements are required to be traceable to either NBS SRMs or other gas standards which have been approved by the EPA Administrator (3). SRMs were developed to provide more accurate standards than were available from commercial sources at the time (4). Since their introduction, they have become accepted as benchmarks for air quality measurements. This acceptance created a demand for SRMs which occasionally exceeds NBS production capacity and, at times, NBS's inventory of SRMs has been exhausted.

In response to this demand for more high-accuracy standards, NBS and EPA established a traceability procedure by which specialty gas producers can prepare and analyze standards whose accuracy approaches that of SRMs (5,6). These standards are called Certified Reference Materials (CRMs). The traceability procedure details the criteria and requirements by which a specialty gas producer can produce certain gaseous mixtures for use as CRMs and then certify them as being directly traceable to NBS gaseous SRMs. The purchaser of a CRM is assured that its accuracy is high because (1) the general technical procedure for preparing and analyzing CRMs has been specified by NBS; (2) the analyses of the CRMs use SRMs as their reference standards; (3) the producer's analytical results are verified by an EPA-coordinated, independent performance audit; and (4) both the producer's and the auditor's analytical results must be reviewed and approved by NBS before the gas mixtures can be certified for sale as CRMs.

EPA regulations allow CRMs to be used as equivalents of SRMs for ambient air quality surveillance (7) and for continuous emission monitoring systems (8). Similarly, CRMs have been approved for use in new motor vehicle certification (9) and in vehicle inspection and maintenance programs (10).

Since November 1980, the Research Triangle Institute (RTI) has been the EPA-coordinated, independent auditor for the CRM program (11). This work has been performed under various work assignments of EPA Contract Numbers 68-02-3431, 68-02-3767, and 68-02-4125. This report summarizes the CRM program in general and the audit program specifically.

As of October 1986, 34 batches of specialty gas producers' calibration standards have satisfied the requirements for CRMs. These CRMs contain carbon monoxide in nitrogen, carbon monoxide in air, nitric oxide in nitrogen, or propane in nitrogen. Additionally, NBS and EPA have established procedures for the production of CRMs that contain sulfur dioxide in nitrogen, or propane in air. A procedure for the production of oxygen in nitrogen CRMs is under development. EPA maintains a list of all batches of CRMs that have been approved for sale (12).

SECTION 2

CONCLUSIONS

This report has dealt with the performance audit program for CRMs. To date, specialty gas producers have prepared and analyzed 36 batches of CRMs containing carbon monoxide in nitrogen, carbon monoxide in air, nitric oxide in nitrogen, or propane in nitrogen. Acceptable agreement was found between the producers' analytical results and the auditor's analytical results for all 72 audit samples. The mean absolute value for the percent difference between the two sets of results is 0.18 percent relative. The maximum absolute value of the percent difference is 0.60 percent relative. These data demonstrate that specialty gas producers can prepare and analyze CRMs with a high degree of accuracy.

These data for CRMs can be compared with similar data for SRMs to gain some perspective on the accuracy of SRMs. The following statement is taken from a paper which describes the first batches of CRMs that were prepared. These CRMs and the SRMs that were used as reference standards consisted of 50 parts per million (ppm) carbon monoxide in nitrogen.

> "It is estimated that the uncertainty of an SRM, consisting of carbon monoxide in nitrogen, relative to any other SRM of the same composition and nominal concentration does not exceed 0.1 ppm or 0.2 % relative." (5)

Therefore, it would appear that the uncertainty of CRMs approaches that of SRMs.

Prior to the audits, NBS sent "unknowns" to RTI to assess RTI's analytical performance. Acceptable agreement was found between RTI's analytical results and NBS's certified concentrations for 22 unknowns which have been analyzed to date. The mean absolute value of the agreement is 0.17 percent relative. The maximum absolute value of the agreement is 0.56 percent relative. These data demonstrate that audits can be conducted with a high degree of accuracy.

An informal study to estimate the long-term stability of CRMs was conducted by RTI which involved the reanalysis of nine previously audited CRMs. The times between the original audits and the reanalysis ranged from 11 to 25 months. The mean absolute value of the concentration change is 0.16 percent relative. The largest concentration change observed is 0.29 percent relative. These data suggest that CRMs remain stable throughout their two-year certification periods.

SECTION 3

PROCEDURES FOR THE PRODUCTION OF CRMs

THE CRM PRODUCER

The NBS/EPA traceability procedure (6) specifies, in general terms, how specialty gas producers may prepare and analyze a batch of candidate CRMs. Although the specific details are left to the CRM producer to decide, enough has been spelled out in the procedure to assure that a producer can attain adequate accuracy. Some of the significant elements of the procedure are listed below:

- An SRM must be used as the reference standard for the analysis of the CRM batch. It should be noted that NBS allows one cylinder from the batch to be used as an intermediate, internal standard. The use of an internal standard allows conservation of the SRM. It is important that the calibration chain between the SRM and the CRM be as short as possible to reduce the CRM's total uncertainty;

- When a CRM batch is produced, the batch mean concentration must lie within $\pm$ 1 percent relative of the concentration of the SRM to be used as the reference standard. As a result, error due to inadequate instrumental linearity will be reduced;

- Each CRM batch must contain at least 10 cylinders having identical concentrations. The batch must be large enough to allow valid statistical inferences to be drawn concerning the homogeneity of the batch and the concentration of individual cylinders in the batch;

- The CRM producer must demonstrate that the batch is homogeneous. Homogeneity can be demonstrated by comparing the distribution of the measured concentrations for the entire batch with the precision of the analytical method;

- The CRM producer must demonstrate that the batch is stable by performing two analyses of the batch that are separated by at least a month's time. Nitric oxide in nitrogen CRMs are required to have a 2-month incubation period. If no appreciable concentration change has occurred, the batch is considered to be stable.

Table 1 gives an example of a CRM producer's analytical results for a batch of carbon monoxide in nitrogen CRMs. The reference SRM has a concentration of 47.1 ppm. It can be seen that the batch's overall mean concentration is very close to that value. This batch was found to be homogeneous by comparing the standard deviations of the batch and internal standard measurements (e.g., 0.137 ppm for the first analysis of the batch and 0.076 for the first analyses of the internal standard). The batch was found to be stable because the "paired difference" test indicated that the differences between the first and second analyses were not statistically significant.

TABLE 1. PRODUCER'S ANALYTICAL RESULTS FOR A BATCH OF 47.2 PARTS PER MILLION CARBON MONOXIDE IN NITROGEN CRMs

Sample	First Analysis Concentration (ppm)	Second Analysis Concentration (ppm)	Difference (ppm)	Mean Concentration (ppm)
1[a]	47.197[b]	47.206[c]	+0.009	47.202
2	47.149	47.239	+0.090	47.194
3	46.941	47.167	+0.226	47.054
4	47.197	47.144	-0.053	47.170
5	47.178	47.201	+0.023	47.190
6	47.244	47.169	-0.075	47.206
7	47.263	47.167	-0.096	47.215
8	47.150	47.255	+0.105	47.202
9	46.847	47.350	+0.503	47.098
10	47.055	47.308	+0.253	47.182
11	47.282	47.192	-0.090	47.237
Mean	47.137	47.218	+0.081	47.177
Std. dev.	0.137	0.064	0.184	0.054

[a] Internal standard for the batch.

[b] The standard deviation for 11 measurements of the internal standard during the first analysis was 0.076 ppm.

[c] The standard deviation for 9 measurements of the internal standard during the second analysis was 0.114 ppm.

An example of a batch which did not meet the CRM requirements is given in Table 2 (13). The CRM producer analyzed a batch of nitric oxide in nitrogen CRMs on three separate occasions. NBS reviewed these data and made the following assessment:

> "The data shows that several samples have decreased in concentration from one analysis to the next. This behavior suggests that some samples are unstable, but it would be difficult to prove that the lot is either stable or unstable." (13)

Because of these stability questions, this batch has not been certified as meeting the requirements for CRM's.

After a CRM producer is satisfied that a batch is homogeneous and stable, a letter containing the analytical results is sent to NBS for review. Additionally, the EPA-designated auditor is sent a letter which states that a CRM batch is available to be audited.

THE PERFORMANCE AUDIT PROGRAM FOR CRMs

The purpose of the EPA Performance Audit Program is to provide NBS with an independent set of analytical results for a CRM batch which NBS will use to verify the producer's analytical results. The audit is conducted on two samples from the batch which are selected at random by EPA. These samples are analyzed at an independent laboratory (in this case, RTI) which is funded by EPA. If the auditor's analytical results confirm the producer's analytical results for the two samples, then NBS can conclude that the producer's analytical results are accurate for the two samples and, by inference, for the remainder of the batch. The general features of the audit have been specified in the NBS/EPA traceability procedure (6) with the details being left to the discretion of the auditor. Nevertheless, enough is spelled out in the traceability procedure to assure that the auditor can attain adequate accuracy. Some of the significant features of the audit procedure are listed below:

- The auditor randomly selects the two samples from the batch that will be audited. The producer is not aware which cylinders will be audited until after it has sent its analytical results to NBS.

- The auditor is not told the producer's analytical results until after the audit results have been sent to NBS. Thus, the auditor cannot subjectively interpret the audit data based on knowledge of the producer's analytical results.

- An SRM must be used by the auditor as the reference standard for the audit measurements. Thus, the auditor's and the producer's reference standards are tied to the same primary standards at NBS and the two sets of measurements may be validly compared.

TABLE 2. PRODUCER'S ANALYTICAL RESULTS FOR A BATCH OF 1000 PARTS PER MILLION NITRIC OXIDE IN NITROGEN STANDARDS WHICH DID NOT SATISFY CRM REQUIREMENTS (Source: Reference 13)

Sample No.	Concentration December 1981 (ppm)	Concentration January 1982 (ppm)	Concentration June 1982 (ppm)	Difference June-Dec. (ppm)
1	954.1	953.3	951.6	-2.5
2	954.1	955.4	953.6	-0.5
3	953.8	954.0	953.5	-0.3
4	953.3	953.8	956.7	+3.4
5	955.0	954.7	950.8	-4.2
6	953.8	953.6	950.0	-3.8
7	953.7	953.1	952.4	-1.3
8	953.0	954.0	955.7	+2.7
9	954.4	953.5	952.2	-2.2
10	955.4	954.9	954.2	-1.2
11	953.9	955.4	954.7	+0.8
12	955.0	955.4	955.5	+0.5
13	955.6	954.6	954.7	-0.9
14	954.2	955.7	955.6	+1.4
15	954.5	955.4	954.7	+0.2
16	954.6	955.6	956.7	+2.1
17	954.3	953.5	961.5	-2.8
18	953.3	954.5	953.8	+0.5

- The auditor must make at least 10 replicate measurements of each audit sample. This allows the precision of these measurements to be determined. The audit must be repeated if the standard deviation of the measurements exceeds 0.5 percent relative.

The detailed audit procedures and analytical methods used by RTI are adapted from those used by NBS in its analyses of SRMs (14). The analytical instrumentation used for the CRM audits is listed in Table 3. In general, the analytical procedure is identical for each of the measurement parameters. The contents of the audit samples, the reference SRM or the zero gas are fed without dilution through the analytical instrument by means of the cylinder's pressure alone. Each cylinder is connected through a pressure regulator and a solenoid valve into a common sampling manifold and needle valve. A pressure gauge is mounted in the manifold upstream of the needle valve. Each regulator's output pressure is adjusted to produce the same reading on the manifold pressure gauge. This process assures that the sample flow rate through the instrument is the same for each cylinder. The solenoid valves control which cylinder is being analyzed and are sequentially actuated by a digital timer. The measurement cycle is zero-SRM-CRM(1)-CRM(2), as is illustrated in Figure 1. This cycle is repeated at least ten times. Each measurement in the cycle has a period from 5 to 15 minutes, depending on the measurement parameter. Longer measurement periods are used for noisier signals. The voltage output from the instrument is recorded at regular intervals (e.g., 10 seconds) by a data logger. The data logger calculates a mean voltage for the last half or last third of each measurement period. The use of a data logger reduces the uncertainty due to short-term noise by producing a more precise value than could be obtained from an instantaneous voltage reading. A strip chart recorder is used to verify that the instrument's response is stable prior to the start of data collection. An instrument zero value and an instrument sensitivity are determined for each CRM measurement by interpolation between the two adjacent zero measurements and the two adjacent SRM measurements. This reduces the uncertainty due to long-term zero and span drifts. The sensitivities are multiplied by the zero-corrected mean CRM voltages to yield measured CRM concentrations.

One variation from this analytical procedure is used for nitric oxide CRM audits. Because the chemiluminescence instrument uses a high-vacuum reaction chamber and because the instrument sensitivity is an inverse function of the absolute pressure in the reaction chamber, the gas cannot be pushed through the instrument. Instead, sample flows through the sampling manifold at atmospheric pressure at a rate that is slightly higher than the instrument requires. The instrument pumps what it needs from the sampling manifold and the excess is vented. It should also be noted that the oxides of nitrogen (i.e., nitric oxide and nitrogen dioxide) concentration is measured several times during an audit of nitric oxide CRMs. This allows calculation of the sample's nitrogen dioxide concentration which the NBS/EPA traceability procedure allows to be present at levels, which may not exceed 1 percent of the nitric oxide concentration.

TABLE 3. ANALYTICAL INSTRUMENTATION FOR CRM PERFORMANCE AUDITS

Measurement Parameter	Analytical Instrumentation	Analytical Principle
Carbon Monoxide (0 to 1000 ppm)	Bendix 8501-5CA	Non-dispersive Infrared Spectroscopy
Carbon Monoxide (0.1 to 1 %)	Horiba PIR-2000	Non-dispersive Infrared Spectroscopy
Carbon Monoxide (1 to 10 %)	Perkin-Elmer 3920B	Gas Chromatography with a Thermal Conductivity Detector
Sulfur Dioxide	Thermo-Electron 40	Pulsed Ultraviolet Fluorescence Spectroscopy
Nitric Oxide	Thermo-Electron 10AR	Chemiluminescence Spectroscopy
Propane	Perkin-Elmer 3920B	Gas Chromatography with a Flame Ionization Detector

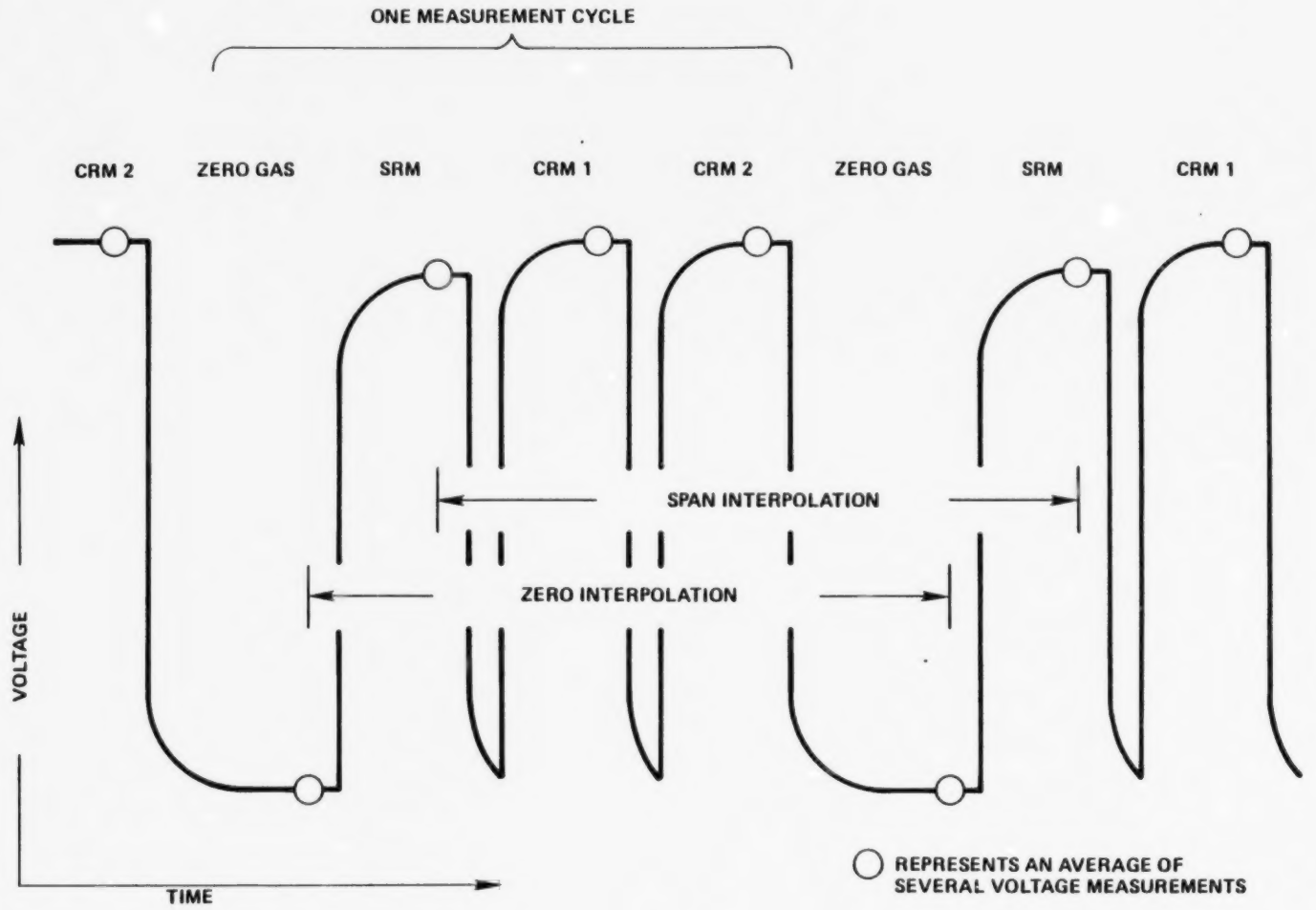

Figure 1. Stylized representation of a portion of a strip chart trace from a performance audit of Certified Reference Materials.

A second variation from the normal analytical procedure is used for propane or high concentration carbon monoxide CRM audits. The gas chromatograph requires the use of a calculating integrator in the place of the data logger. The digital timer controls the sampling valve as well as the solenoid valves. At least five injections are made during each measurement period. Only the injections from the latter part of the measurement period are used to calculate mean area counts.

Either immediately before or immediately after the audit, the linearity of the analytical instrumentation is checked. The reference SRM, the zero gas, and several other SRMs of differing concentrations are measured in the same manner as the audit samples. Normally, three or more replicate measurements of each SRM are made to improve precision. The deviation of each measurement from the linear regression line drawn through all the measurements is used as an index of linearity. Although the NBS/EPA traceability procedure has not established specific acceptance limits for linearity, data demonstrating that the instrumentation is linear reduces the uncertainty of the audit measurements.

During and immediately after a CRM audit, the measured data and ancillary information are transferred from the data logger/integrator output and the strip chart to a bound laboratory notebook. The physical records are then stored in the auditor's project files. The calculation of interpolated zero values, interpolated sensitivities, and measured CRM concentrations are performed in the notebook. A mean and a standard deviation for the ten or more measured CRM concentrations are then calculated and recorded in the notebook. Finally, a statistical analysis of the linearity check data is performed and recorded in the notebook. All these calculations are performed by the auditor.

The auditor then prepares a written report of the audit. All mean voltages for the audit samples and the linearity check standards are included in the report. The procedures taken in calculating the mean CRM concentration are explicitly shown. The report also includes information concerning the analytical instrumentation and the reference SRMs and presents the statistical analysis of the linearity check data. After this report has been prepared, it is sent to the RTI Quality Assurance Official for review and approval. The approved report is then sent to NBS and the EPA Project Officer.

Earlier in this section, a producer's analytical results for a batch of 47.2 ppm carbon monoxide in nitrogen CRMs were presented in Table 1. The corresponding audit results for the same batch are given in Table 4. Samples 5 and 7 were chosen at random to be audited. For Sample 5, the mean audit value of 47.276 ppm is within 0.18 percent relative of the mean producer value of 47.190 ppm. For Sample 7, the mean audit value of 47.286 ppm is within 0.15 percent relative of the mean producer value of 47.215 ppm. Given the total uncertainty for both the producer's and the auditor's analytical results, a statistically significant difference does not exist between the two sets of results.

TABLE 4. AUDITOR'S ANALYTICAL RESULTS FOR TWO SAMPLES FROM A BATCH OF 47.2 PARTS PER MILLION CARBON MONOXIDE IN NITROGEN CRMs

Analysis Number	Sample 5 Concentration (ppm)	Sample 7 Concentration (ppm)
1	47.275	47.278
2	47.281	47.281
3	47.271	47.266
4	47.266	47.294
5	47.289	47.310
6	47.270	47.289
7	47.275	47.288
8	47.293	47.310
9	47.276	47.278
10	47.269	47.267
Mean	47.276	47.286
Std. dev.	0.009	0.015

NBS'S REVIEW OF THE RESULTS

After NBS has received the producer's analytical results and the EPA-coordinated audit results, both sets of results are reviewed. The producer's analytical results must demonstrate that the batch is homogeneous and stable. The batch is judged to be homogeneous if the standard deviation of the producer's batch measurements is not significantly different from the standard deviation of the internal standard measurements. The batch is judged to be stable if the statistical distribution of differences between the producer's first and second analyses for individual cylinders is random and is not significantly different from zero. The concentration of the batch is judged to have been accurately measured if the audit results are not significantly different from the producer's analytical results.

In the event that NBS is not convinced that the batch is homogeneous, stable, and accurately measured, NBS may request that the producer perform additional measurements of the batch, or that the auditor perform additional measurements of the audit samples. Alternatively, NBS may have the auditor send the audit samples to NBS for an analysis. Such analyses have been necessary twice in the history of the program. The results of these analyses are given in Table 5. In these two cases, NBS's results confirmed the auditor's results.

If NBS is satisfied that a particular batch has satisfied the requirements for CRMs, it notifies EPA and the producer by letter. This letter gives measured concentrations for each member in the batch and compares the producer's analytical results with the audit results. It also gives a total uncertainty associated with the measured concentrations.

In general, NBS remains the final arbiter concerning the homogeneity, stability, and accuracy of each CRM batch. The active participation of NBS in the production of CRMs ensures their credibility as reliable substitutes for SRMs.

TABLE 5. COMPARISON OF PRODUCER'S, AUDITOR'S AND NBS'S ANALYTICAL RESULTS FOR TWO SETS OF CARBON MONOXIDE IN NITROGEN AUDIT SAMPLES

Producer's Results (ppm)	Auditor's Results (ppm)	Percent Difference[a] (percent relative)	NBS's Results (ppm)	Difference[b] (percent relative)
9.91	9.94	+ 0.30	9.94	0.00
9.89	9.95	+ 0.61	9.94	+0.10
4698	4716	+ 0.38	4714	+0.04
4702	4708	+ 0.13	4710	-0.04

[a] $\text{Percent Difference} = 100 \left[\frac{\text{Auditor's Results} - \text{Producer's Results}}{\text{Producer's Result}} \right]$

[b] $\text{Percent Difference} = 100 \left[\frac{\text{Auditor's Results} - \text{NBS's Results}}{\text{NBS's Results}} \right]$

SECTION 4

CRM STABILITY AND RECERTIFICATION

During the development of SRM's, NBS found that the concentrations of carbon monoxide, nitric oxide, sulfur dioxide, and propane mixtures contained in aluminum cylinders were stable for periods of two or more years. Accordingly, the original NBS traceability procedure for CRMs specified that a CRM batch may be certified for a period of two years following the batch's second analysis. If no significant concentration changes were found between the first and second analyses, then it was highly probable that the batch would remain stable during the two-year certification period. However, a batch could not be given an unlimited certification period. A concentration change may be occurring in a CRM which, over the course of two years, may not exceed the uncertainty of the CRMs' certified concentration. However, such a change may exceed the uncertainty over greater periods of time.

As CRMs were beginning to be produced, NBS and EPA decided to verify that the CRM's concentrations would remain stable through their two-year certification period. As a result, an informal long-term stability study was conducted with the cooperation of the CRM producers. NBS and EPA identified nine previously-approved CRM batches as being of particular interest. The producers were contacted with the request that one of the two audit samples from each batch be returned to the auditor for reanalysis. During the winter of 1983, nine audit samples were reanalyzed. The times between the original audit and the long-term stability study reanalysis range from 11 to 25 months. The results of these measurements are listed in Table 6 and are presented as a histogram in Figure 2. In general, these data suggest that no significant concentration changes had occurred in these samples. The mean absolute value of the changes is 0.16 percent relative. The largest change observed is 0.29 percent relative after 25 months, which is well within the total uncertainty of 1 percent relative for the sample's certified concentration. One cannot make broad statements concerning the long-term stability of all CRMs based on measurements of a few samples; nevertheless, these data are encouraging and suggest that CRMs remain stable throughout their certification periods.

In 1984, NBS and EPA developed an appendix to the traceability procedure which allows CRM producers to recertify CRMs after their original two-year certification period has expired. The producers may take one of two approaches in the recertification. The first approach is to extend the certification of all unsold CRMs in a batch for a specified period following reanalysis of these samples (i.e., batch recertification). The second approach is to certify individual CRMs in a batch for a specified period, beginning at the time of sale of each CRM to a purchaser (i.e., "date-of-sale" certification). In both cases, a reanalysis must be performed and the analytical results must be submitted to NBS for review and approval.

TABLE 6. DATA FROM LONG-TERM STABILITY STUDY OF CRMs

CRM Composition	Nominal CRM Concentration	Auditor Analysis Date	Auditor Measured Concentration	Change[a] (percent relative)
Carbon monoxide in nitrogen	50 ppm	January 1982	47.29 ppm	
		February 1983	47.34 ppm	+ 0.11
	50 ppm	January 1981	48.49 ppm	
		February 1983	48.63 ppm	+ 0.29
	50 ppm	January 1981	47.19 ppm	
		February 1983	47.31 ppm	+ 0.25
	250 ppm	August 1981	243.92 ppm	
		March 1983	244.25 ppm	+ 0.14
	250 ppm	January 1982	244.21 ppm	
		March 1983	244.18 ppm	- 0.01
	1000 ppm	January 1982	971.8 ppm	
		March 1983	971.3 ppm	- 0.05
	1000 ppm	January 1982	944.6 ppm	
		March 1983	947.2 ppm	+ 0.28
Carbon monoxide in air	43 ppm	January 1982	42.70 ppm	
		February 1983	42.77 ppm	+ 0.16
Nitric oxide in nitrogen	500 ppm	March 1982	470.2 ppm	
		February 1983	469.4 ppm	- 0.17

[a] $\text{Change} = 100 \left[\frac{\text{Second analysis concentration} - \text{First analysis concentration}}{\text{First mean concentration}} \right]$

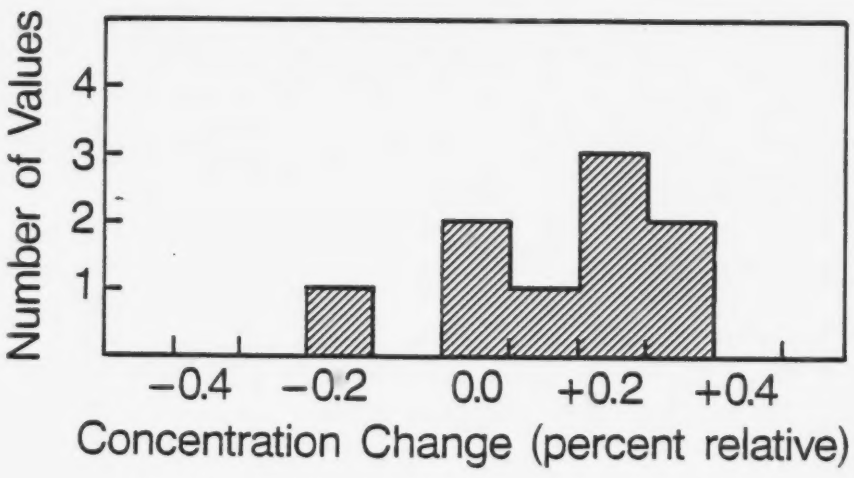

Figure 2. Frequency distribution for the concentration change between the first and second analyses of selected CRM audit samples.

For batch recertification, all unsold CRMs are reanalyzed in a manner identical to the second analysis of the original certification. If the reanalysis demonstrates that the CRMs' concentration has not changed from that of the original certification, then the certification period may be extended for up to two years after the reanalysis date. As of this time, seven batches of CRMs have been recertified using this approach. One of these seven batches contains 50 ppm carbon monoxide in nitrogen. It was originally certified in May 1981 and was recertified in July 1983. During these 26 months, none of the 12 CRMs in the batch exhibited a significant concentration change. The original and reanalyzed concentrations for this batch are given in Table 7. Another of the seven CRM batches contains 43 ppm carbon monoxide in air. It was originally certified in February 1982 and was recertified in July 1984. During these 28 months, nine of the ten CRMs in the batch did not exhibit a significant concentration change and were recertified. The remaining CRM showed signs of instability and could not be recertified. The original and reanalyzed concentrations for this batch are given in Table 8. These data suggest that, in general, CRMs remain stable through their certification period and may be recertified with confidence.

For date-of-sale certification, all CRMs in a batch are analyzed on three separate occasions over a six-month period prior to their original certification. At 18 months and 30 months after the batch's preparation, 20 percent (or at least 4) of the batch must be reanalyzed in a manner identical to the original analyses. The reanalysis results must be submitted to NBS for review. If none of the results suggest that a significant concentration change has occurred, an individual CRM may be certified for up to two years from the date of its sale. As of this time, no CRM batches have been prepared and analyzed for date-of-sale certification.

TABLE 7. RECERTIFICATION DATA FOR A BATCH OF CRMs CONTAINING 50 PPM CARBON MONOXIDE IN NITROGEN

Original[a] Concentration (ppm)	Reanalyzed[b] Concentration (ppm)	Change[c] (percent relative)
47.18	47.16	-0.04
47.18	47.17	-0.02
47.17	47.25	+0.17
47.20	47.17	-0.06
47.16	47.13	-0.06
47.21	47.12	-0.19
47.17	47.11	-0.13
47.17	47.22	+0.11
47.18	47.18	0.00
47.16	47.12	-0.08
47.19	47.22	+0.06
47.17	47.15	-0.04
	Mean	-0.02

[a] Batch originally certified in May 1981.

[b] Batch recertified in July 1983.

[c] $\text{Change} = 100 \left[\frac{\text{Reanalyzed Concentration} - \text{Original Concentration}}{\text{Original Concentration}} \right]$

TABLE 8. RECERTIFICATION DATA FOR A BATCH OF CRMs CONTAINING 43 PPM CARBON MONOXIDE IN AIR

Original[a] Concentration (ppm)	Reanalyzed[b] Concentration (ppm)	Change[c] (percent relative)
42.3	42.3	0.00
42.4	42.3	-0.24
42.4	42.3	-0.24
42.3	42.4	+0.24
42.3	42.3	0.00
42.3	42.3	0.00
42.3	42.4	+0.24
42.3	42.3	0.00
42.3	42.3	0.00
42.4	42.2[d]	-0.47
	Mean	-0.05

[a] Batch originally certified in February 1982.

[b] Batch recertified in July 1984.

[c] $\text{Change} = 100 \left[\frac{\text{Reanalyzed Concentration} - \text{Original Concentration}}{\text{Original Concentration}} \right]$

[d] This sample showed signs of instability and could not be recertified.

SECTION 5

QUALITY ASSURANCE FOR THE CRM AUDIT PROGRAM

Quality assurance procedures for the CRM Audit Program are documented in its Quality Assurance Project Plan (15). This document received EPA approval in August 1984 and presents a detailed description of the quality assurance aspects of the program. Analytical and calibration procedures are described in this report; also documented are the project's quality assurance objectives for precision, accuracy, completeness, representativeness and comparability.

The most important quality assurance objective for the program is accuracy. The use of SRM's as reference standards during the audits is the primary means to ensure accuracy. Additionally, there are two means to obtain an external evaluation of the accuracy of the audit program. The first means is the definitive analyses which NBS performs when there is a significant disagreement between the producer's analytical results and the audit results. As was shown in Section 3, NBS's results confirmed the audit results for two CRM batches.

The second means to evaluate the accuracy of the audit program is the analysis of "unknowns" by the auditor. Before the CRM producers begin to produce a particular class of CRMs, NBS evaluates the auditor's analytical ability to perform audits of this class by sending unknowns for analysis. These unknowns are well-characterized SRMs from NBS's inventory whose certified concentrations are unknown to the auditor. They are analyzed in the same manner as audit samples. There must be reasonably close agreement (i.e., percent difference) between the auditor's analytical results and the NBS-certified concentrations. As of October 1986, analyses have been conducted for 22 unknowns containing carbon monoxide in nitrogen, nitric oxide in nitrogen, sulfur dioxide in nitrogen, or propane in nitrogen. The results of these analyses are summarized in Table 9. Acceptable agreement was found for all 22 unknowns. The closest percent difference is 0.00 percent relative and the poorest percent difference is -0.56 percent relative. The mean of the absolute values of the percent difference is 0.17 percent relative. A frequency distribution of the absolute values of the percent differences is given in Figure 3. This level of agreement demonstrates the ability of the auditor to measure gaseous calibration standards with a high degree of accuracy. Prior to any audits, this knowledge allowed EPA and NBS to implement the audit program with some degree of confidence.

TABLE 9. COMPARISON OF AUDITOR MEASURED VALUES WITH NATIONAL BUREAU OF STANDARDS CERTIFIED VALUES FOR "UNKNOWNS"

"Unknown" SRM Composition	Nominal SRM Concentration (ppm)	NBS Certified Value (ppm)	Auditor Measured Value (ppm)	Percent Difference[a] (percent relative)
Carbon monoxide in nitrogen	50	44.9	44.77	-0.29
	50	45.3	45.29	-0.02
	100	93.6	93.88	+0.30
	250	243.7	243.66	-0.02
	500	476.	475.85	-0.03
	1000	956.	953.16	-0.30
Nitric oxide in nitrogen	50	47.8	47.82	+0.04
	100	96.4	96.53	+0.13
	250	235.4	235.23	-0.07
	500	462.0	461.61	-0.08
	1000	957.	957.27	+0.03
Sulfur dioxide in nitrogen	50	44.95	44.70	-0.56
	100	95.1	95.10	0.00
	500	464.5[b]	463.1	-0.30
	1000	940.	939.3	-0.07
	1425	1428.	1431.	+0.21
	2375	2316.	2322.	+0.26
	3500	3122.	3138.2	+0.52
Propane in nitrogen	250	244.2	244.3	+0.04
	1000	973.7	973.4	-0.03
	5000	4880.	4897.	+0.35
	20000	19620.	19652.	+0.16

[a] $\text{Percent Difference} = 100 \left[\frac{\text{RTI measured value} - \text{NBS certified value}}{\text{NBS certified value}} \right]$

[b] Mean of original certified value of 459 ppm and a value of 470 ppm measured at NBS after the auditor's analysis. This SRM's concentration shifted as the cylinder pressure decreased.

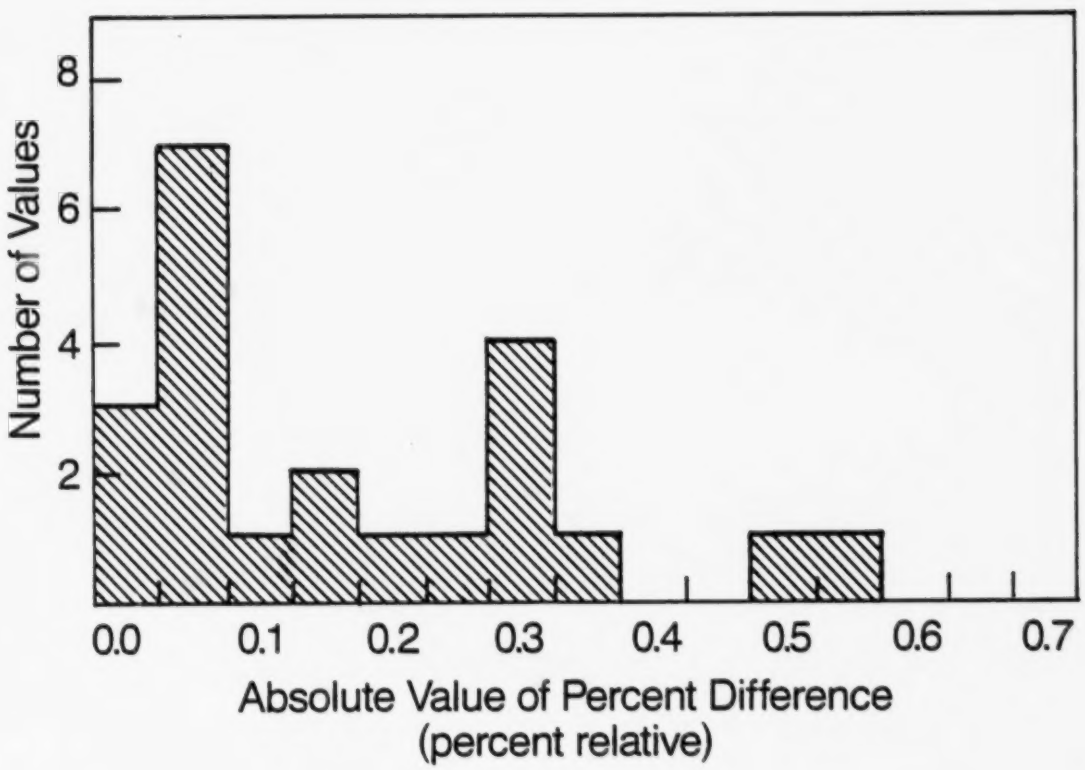

Figure 3. Frequency distribution for the percent difference between RTI measured values and NBS certified values for "unknowns".

SECTION 6

SUMMARY OF CRM AUDITS

As of October 1986, audits have been performed on 36 candidate CRM batches containing carbon monoxide in nitrogen, carbon monoxide in air, nitric oxide in nitrogen, or propane in nitrogen. A chronological summary of these audits is given in Table 10. For all 36 batches, acceptable agreement was obtained between the producer's measured values and the audit results. However, two of these batches could not be certified because of problems not associated with the audit (i.e., batch instability and producer's analytical precision problems). The producer's measured values for all carbon monoxide in nitrogen CRM batches are compared with the audit results in Table 11. Similar comparisons are made in Table 12 for carbon monoxide in air CRM batches, in Table 13 for nitric oxide in nitrogen CRM batches, and in Table 14 for propane in nitrogen CRM batches. The frequency distribution of the absolute value of the percent difference between the producer's and the auditor's measured values is given in Figure 4.

In general, the absolute value of the percent difference has been within 0.5 percent relative. The mean absolute value of the percent difference for the 72 audit samples is 0.18 percent relative. The maximum absolute value of the percent difference is 0.60 percent relative. This level of agreement is within the limits set for the program and demonstrates that speciality gas producers can prepare and analyze CRMs with a high degree of accuracy.

The data in Tables 11 through 13 can also be used to give some indication of the precision of the audits. The coefficient of variation (CV) will be used as an index of precision. Nondispersive infrared analyzers were used for carbon monoxide CRM audits at concentrations of 1 percent or less. The 44 audit samples in this concentration range had a mean CV of 0.05 percent relative and a maximum CV of 0.14 percent relative. A gas chromatograph with a thermal conductivity detector was used for carbon monoxide CRM audits at concentrations of 2 percent or greater. The 10 audit samples in this concentration range had a mean CV of 0.35 percent relative and a maximum CV of 0.56 percent relative. A chemiluminescence analyzer was used for nitric oxide CRM audits. The 10 nitric oxide audit samples had a mean CV of 0.09 percent relative and a maximum CV of 0.19 percent relative. A gas chromatograph with a flame ionization detector was used for propane CRM audits. The four propane audit samples had a mean CV of 0.19 percent relative and a maximum CV of 0.27 percent relative. These CVs are within the limits specified by the NBS/EPA traceability document, with the exception of the high concentration carbon monoxide measurements, whose CVs need some improvement.

TABLE 10. CHRONOLOGICAL SUMMARY OF CRM AUDITS AND CURRENT STATUS OF CRM BATCHES

Audit Date	CRM Producer	Certified Reference Material	Batch Status
Jan 81	Scott	50 ppm Carbon Monoxide in Nitrogen	Consumed
Jan 81	Airco	50 ppm Carbon Monoxide in Nitrogen	Consumed
May 81	Airco	500 ppm Carbon Monoxide in Nitrogen	Consumed
May 81	Airco	100 ppm Carbon Monoxide in Nitrogen	Consumed
June 81	Airco	25 ppm Carbon Monoxide in Nitrogen	Consumed
Aug 81	Airco	250 ppm Carbon Monoxide in Nitrogen	Consumed
Dec 81	Airco	43 ppm Carbon Monoxide in Air	Out of Cert.(1)
Jan 82	Scott	250 ppm Carbon Monoxide in Nitrogen	Out of Cert.(1)
Jan 82	Matheson	50 ppm Carbon Monoxide in Nitrogen	Consumed
Jan 82	Scott	43 ppm Carbon Monoxide in Air	Out of Cert.(1)
Jan 82	Airco	1000 ppm Carbon Monoxide in Nitrogen	Recertified
Jan 82	Scott	1000 ppm Carbon Monoxide in Nitrogen	Out of Cert.(1)
Feb 82	Airco	2500 ppm Carbon Monoxide in Nitrogen	Recertified
Feb 82	Airco	8 % Carbon Monoxide in Nitrogen	Recertified
Mar 82	Airco	500 ppm Nitric Oxide in Nitrogen	Consumed
Mar 82	Airco	1000 ppm Nitric Oxide in Nitrogen	Blown Down
Mar 82	Scott	10 ppm Carbon Monoxide in Nitrogen	Out of Cert.(1)
Apr 82	Scott	25 ppm Carbon Monoxide in Nitrogen	Out of Cert.(1)
Apr 82	Airco	5000 ppm Carbon Monoxide in Nitrogen	Recertified
May 82	Airco	100 ppm Nitric Oxide in Nitrogen	Consumed
May 82	Airco	10 ppm Carbon Monoxide in Nitrogen	Blown Down
July 82	Scott	2500 ppm Carbon Monoxide in Nitrogen	Out of Cert.(1)
July 82	Scott	5000 ppm Carbon Monoxide in Nitrogen	Out of Cert.(1)
Aug 82	Airco	250 ppm Nitric Oxide in Nitrogen	Consumed
Feb 83	Air Prod.	500 ppm Carbon Monoxide in Nitrogen	Out of Cert.(1)
Feb 83	Scott	250 ppm Nitric Oxide in Nitrogen	Recertified
Apr 83	Matheson	10 ppm Carbon Monoxide in Nitrogen	Consumed
May 83	Air Prod.	50 ppm Carbon Monoxide in Nitrogen	Out of Cert.(1)
Oct 83	Airco	4 % Carbon Monoxide in Nitrogen	Out of Cert.(1)
Oct 83	Air Prod.	1 % Carbon Monoxide in Nitrogen	Reanalyzed(2)
Oct 83	Air Prod.	5000 ppm Carbon Monoxide in Nitrogen	Out of Cert.(1)
Jan 84	Air Prod.	2 % Carbon Monoxide in Nitrogen	Reanalyzed(2)
Jan 84	Air Prod.	8 % Carbon Monoxide in Nitrogen	Reanalyzed(2)
Dec 84	Airco	2 % Carbon Monoxide in Nitrogen	Certified
Sept 85	Air Prod.	5000 ppm Propane in Nitrogen	Certified
Feb 86	Air Prod.	1000 ppm Propane in Nitrogen	Certified

(1) Out of certification CRMs may be recertified using Appendix G of the CRM Procedure Document (6).

(2) This out of certification CRM batch has been reanalyzed by its producer, but the results have not been reported to NBS.

TABLE 11. COMPARISON OF PRODUCER'S MEASURED VALUE WITH AUDIT RESULTS FOR ALL CARBON MONOXIDE IN NITROGEN CRM BATCHES

Nominal CRM Concentration	Producer's Measured Value[a]	Audit Results			Percent Difference (percent relative)[b]
		No. of Values	Mean Measured Value	Standard Deviation	
10 ppm	9.91 ppm[c]	11	9.941 ppm	0.005 ppm	-0.31
	9.89 ppm[c]	11	9.950 ppm	0.014 ppm	-0.60
	9.542 ppm[d]	13	9.535 ppm	0.007 ppm	+0.07
	9.535 ppm[d]	13	9.540 ppm	0.009 ppm	-0.05
	9.806 ppm	15	9.800 ppm	0.010 ppm	+0.06
	9.806 ppm	15	9.800 ppm	0.006 ppm	+0.06
25 ppm	24.28 ppm	10	24.21 ppm	0.01 ppm	+0.29
	24.29 ppm	10	24.23 ppm	0.02 ppm	+0.25
	24.32 ppm	10	24.27 ppm	0.01 ppm	+0.21
	24.32 ppm	10	24.26 ppm	0.01 ppm	+0.25
50 ppm	48.39 ppm	10	48.49 ppm	0.01 ppm	-0.21
	48.42 ppm	10	48.50 ppm	0.01 ppm	-0.16
	47.16 ppm	10	47.19 ppm	0.01 ppm	-0.06
	47.20 ppm	10	47.19 ppm	0.01 ppm	+0.02
	47.19 ppm	10	47.28 ppm	0.01 ppm	-0.19
	47.22 ppm	10	47.29 ppm	0.02 ppm	-0.15
	47.12 ppm	11	47.19 ppm	0.01 ppm	-0.15
	47.16 ppm	11	47.20 ppm	0.01 ppm	-0.08
100 ppm	97.12 ppm	10	96.85 ppm	0.02 ppm	+0.28
	97.22 ppm	10	96.88 ppm	0.02 ppm	+0.35
250 ppm	243.9 ppm	10	243.9 ppm	0.5 ppm	0.00
	244.0 ppm	10	243.9 ppm	0.6 ppm	+0.04
	244.1 ppm	10	244.2 ppm	0.0 ppm	-0.04
	244.0 ppm	10	244.2 ppm	0.1 ppm	-0.08
500 ppm	472.5 ppm	10	473.0 ppm	0.1 ppm	-0.11
	472.9 ppm	10	472.9 ppm	0.1 ppm	0.00
	476.2 ppm	12	474.8 ppm	0.1 ppm	+0.29
	476.1 ppm	12	474.8 ppm	0.1 ppm	+0.27
1000 ppm	946.4 ppm	11	944.6 ppm	0.5 ppm	+0.19
	946.4 ppm	11	944.2 ppm	0.5 ppm	+0.23
	969.8 ppm	11	971.8 ppm	0.5 ppm	-0.21
	970.0 ppm	11	971.0 ppm	0.6 ppm	-0.10
2500 ppm	2404 ppm	10	2414 ppm	1. ppm	-0.41
	2406 ppm	10	2413 ppm	1. ppm	-0.29
	2406 ppm	12	2414 ppm	1. ppm	-0.33
	2404 ppm	13	2413 ppm	1. ppm	-0.37

TABLE 11. (continued)

Nominal CRM Concentration	Producer's Measured Value[a]	Audit Results			Percent Difference (Percent Relative)[b]
		No. of Values	Mean Measured Value	Standard Deviation	
5000 ppm	4683 ppm	11	4690 ppm	2. ppm	-0.15
	4682 ppm	11	4692 ppm	1. ppm	-0.21
	4698 ppm[e]	12	4716 ppm	2. ppm	-0.38
	4702 ppm[e]	12	4708 ppm	1. ppm	-0.13
	4650 ppm	12	4642 ppm	1. ppm	+0.17
	4650 ppm	12	4645 ppm	1. ppm	+0.11
1%	0.955 %	18	0.957 %	0.000 %	-0.21
	0.955 %	18	0.957 %	0.000 %	-0.21
2%	1.963 %	9	1.966 %	0.011 %	-0.15
	1.966 %	9	1.968 %	0.011 %	-0.10
	1.969 %	10	1.967 %	0.007 %	-0.10
	1.967 %	10	1.968 %	0.004 %	+0.05
4%	3.892 %	10	3.911 %	0.017 %	-0.49
	3.890 %	12	3.890 %	0.017 %	0.00
8%	7.71 %	10	7.721 %	0.012 %	-0.1
	7.71 %	9	7.727 %	0.017 %	-0.2
	7.717 %	11	7.696 %	0.022 %	+0.27
	7.700 %	11	7.695 %	0.024 %	+0.06

[a] Based on NBS's letter notifying EPA that the batch has met CRM specifications.

[b] $\text{Percent difference} = 100 \left[\frac{\text{Producer's Value - Audit Value}}{\text{Audit Value}} \right]$

[c] Definitive analysis by NBS indicated that the carbon monoxide concentration in these two samples is 9.94 ppm.

[d] This batch has not been certified due to poor precision for the producer's analytical results.

[e] These values are the producer's original analytical results. After the audit, definitive analysis by NBS established that the carbon monoxide concentrations in these samples are 4714 and 4710 ppm. In NBS's letter to EPA, the producer's measured values were revised to 4706 and 4710 ppm.

TABLE 12. COMPARISON OF PRODUCER'S MEASURED VALUE WITH AUDIT RESULTS FOR ALL CARBON MONOXIDE IN AIR CRM BATCHES

Nominal CRM Concentration	Producer's Measured Value[a]	Audit Results			Percent Difference (percent relative)[b]
		No. of Values	Mean Measured Value	Standard Deviation	
43 ppm	42.36 ppm	11	42.40 ppm	0.01 ppm	-0.09
	42.30 ppm	10	42.45 ppm	0.02 ppm	-0.35
	42.70 ppm	10	42.70 ppm	0.02 ppm	0.00
	42.74 ppm	10	42.69 ppm	0.02 ppm	+0.12

[a]Based on NBS's letter notifying EPA that the batch has met CRM specifications.

[b]Percent difference = $100 \left[\frac{\text{Producer's Value - Audit Value}}{\text{Audit Value}} \right]$

TABLE 13. COMPARISON OF PRODUCER'S MEASURED VALUE WITH AUDIT RESULTS FOR ALL NITRIC OXIDE IN NITROGEN CRM BATCHES

Nominal CRM Concentration	Producer's Measured Value[a]	Audit Results			Percent Difference (Percent Relative)[b]
		No. of Values	Mean Measured Value	Standard Deviation	
100 ppm	93.2 ppm	10	93.70 ppm	0.18 ppm	-0.53
	93.2 ppm	10	93.43 ppm	0.13 ppm	-0.25
250 ppm	243.3 ppm	10	243.3 ppm	0.1 ppm	0.00
	243.7 ppm	10	243.3 ppm	0.2 ppm	+0.16
	236.4 ppm	10	236.4 ppm	0.1 ppm	0.00
	236.4 ppm	10	235.9 ppm	0.2 ppm	+0.21
500 ppm	470. ppm	10	470.3 ppm	0.3 ppm	-0.06
	471. ppm	10	470.2 ppm	0.4 ppm	+0.17
1000 ppm	953.4 ppm[c]	12	957.2 ppm	1.0 ppm	-0.40
	955.1 ppm[c]	10	958.6 ppm	0.9 ppm	-0.37

[a]Based on NBS's letter notifying EPA that the batch has met CRM specifications.

[b] $$\text{Percent difference} = 100 \left[\frac{\text{Producer's Value - Audit Value}}{\text{Audit Value}} \right]$$

[c]This batch has not been certified because of stability problems. The producer's measured value is the mean of the first and second analyses.

TABLE 14. COMPARISON OF PRODUCER'S MEASURED VALUE WITH AUDIT RESULTS FOR ALL PROPANE IN NITROGEN CRM BATCHES

Nominal CRM Concentration	Producer's Measured Value[a]	Audit Results			Percent Difference (Percent Relative)[b]
		No. of Values	Mean Measured Value	Standard Deviation	
1000 ppm	973.5 ppm	9	970.9 ppm	2.6 ppm	+0.27
	972.5 ppm	10	970.3 ppm	2.0 ppm	+0.23
5000 ppm	4835. ppm	10	4837. ppm	7. ppm	-0.04
	4838. ppm	10	4841. ppm	7. ppm	-0.06

[a]Based on verbal information from NBS.

[b] $$\text{Percent Difference} = 100 \left[\frac{\text{Producer's Value} - \text{Audit Value}}{\text{Audit Value}} \right]$$

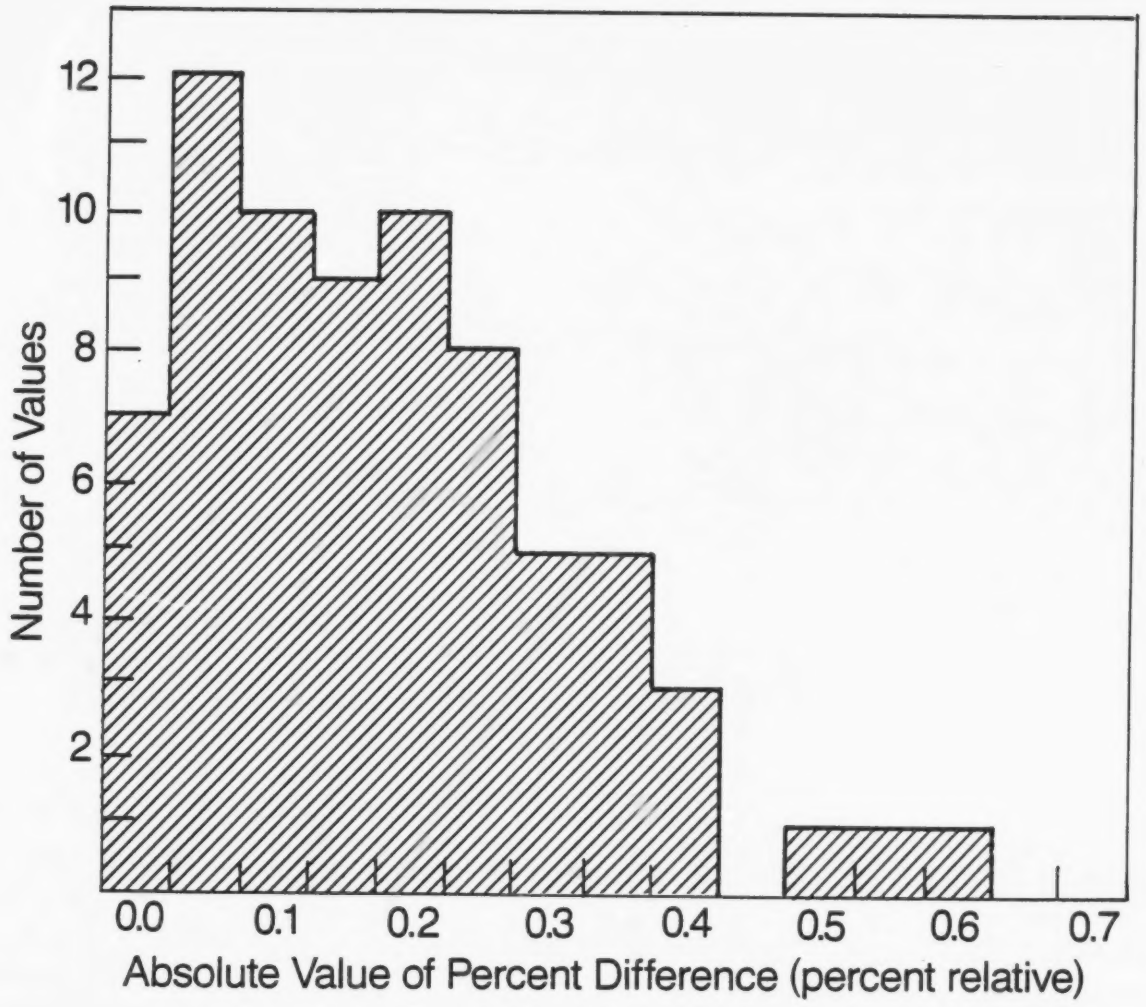

Figure 4. Frequency distribution for the percent difference between producer and auditor measured values for CRM batches.

SECTION 7

CRM AVAILABILITY

A list of all CRM batches that have been approved for sale is given in Table 15. The inclusion of a batch in this list should not be construed to mean that this batch is still in stock or that this batch is within its certification period. The CRM producers should be consulted concerning the current or future availability of any particular CRM. The producers may be contacted at the following addresses and phone numbers:

Airco Industrial Gases
River and Union Landing Roads
Riverton, New Jersey 08077
(609) 829-7878

Air Products and Chemicals, Inc.
P. O. Box 351
Tamaqua, Pennsylvania 18252
(717) 467-2981

Matheson Gas Products
30 Seaview Drive
Secaucus, New Jersey 07094
(201) 867-4100

Scott Specialty Gases
Route 611
Plumsteadville, Pennsylvania 18949
(215) 766-8861

TABLE 15. LIST OF CRM's THAT HAVE BEEN APPROVED FOR SALE

CRM Composition	CRM Concentration	CRM Producer			
		Airco	Air Products	Matheson	Scott
Carbon Monoxide in Nitrogen	10 ppm			Yes	Yes
	25 ppm	Yes			Yes
	50 ppm	Yes	Yes	Yes	Yes
	100 ppm	Yes			
	250 ppm	Yes			Yes
	500 ppm	Yes	Yes		
	1000 ppm	Yes			Yes
	2500 ppm	Yes			Yes
	5000 ppm	Yes	Yes		Yes
	1%		Yes		
	2%	Yes	Yes		
	4%	Yes			
	8%	Yes	Yes		
Carbon Monoxide in Air	43 ppm	Yes			Yes
Nitric Oxide in Nitrogen	100 ppm	Yes			
	250 ppm	Yes			Yes
	500 ppm	Yes			
Propane in Nitrogen	1000 ppm		Yes		
	5000 ppm		Yes		

REFERENCES

1. U.S. Environmental Protection Agency, "National Primary and Secondary Ambient Air Quality Standards," Code of Federal Regulations, Title 40, Chapter 1, Part 50, Washington, DC, Office of the Federal Register, July 1, 1983.

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12. EPA maintains a current list of batches of CRMs that have been approved for sale and their vendors. A copy of this list may be obtained by calling Ms. Katherine A. Powers at (919) 541-2198, or by writing her at the following address: Quality Assurance Division (MD-77), Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

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